STUDY OF THE FORMAMIDE AND DIMETHYLSULFOXIDE COMPLEX USING RAMAN SPECTROSCOPY AND COMPUTATION METHODS

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The Raman spectra of the formamide molecule's C = O vibration band were investigated in this study. Theoretical calculations were carried out on the base of B3LYP 6-311 ++ G. (2d, p). The calculations' results were used to clarify the complexity of the spectral lines. Molecular simulations were conducted from the monomer of the formamide molecule to the pentamer, including for formamide aggregation with dimethyl sulfoxide (DMSO).

Figure 1 depicts the parallel ($I_{\parallel}$) and perpendicular ($I_{\perp}$) components of the Raman spectrum, which belong to the formamide C = O vibration. The maxima of the $I_{\parallel}$ and $I_{\perp}$ constituents do not coincide, the difference is 14 cm^{-1}. According to calculations, different types of dimeric aggregates can be observed in formamide molecules. Dimers are primarily formed as a result of the formation of intermolecular and intramolecular hydrogen bonds between high electrical negativity oxygen and hydrogen atoms, with bond lengths ranging from 1.9 Å to 2.6 Å.

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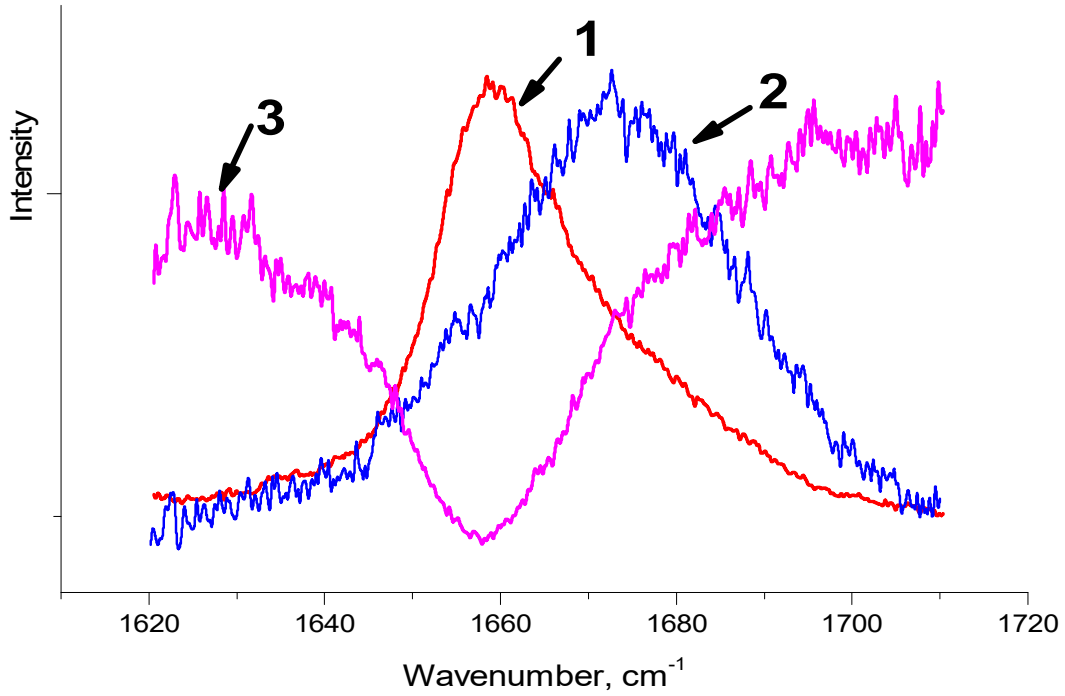

Figure.1. Raman lines of the vibration band C = O of FA: 1) $I_{||}$, 2) $I_{\perp}$, 3) depolarization ratio.

The Raman spectra obtained as a result of the calculations are also presented. The vibrational frequency C = O of the monomer molecule of formamide corresponds to 1783 cm^{-1}, as shown by the spectra. The spectral line shifts towards a low frequency with a maximum of 60 cm^{-1} when viewing complexes up to dimer, trimer, tetromer, and pentomer. Pentamer slides to 1723 cm^{-1}.

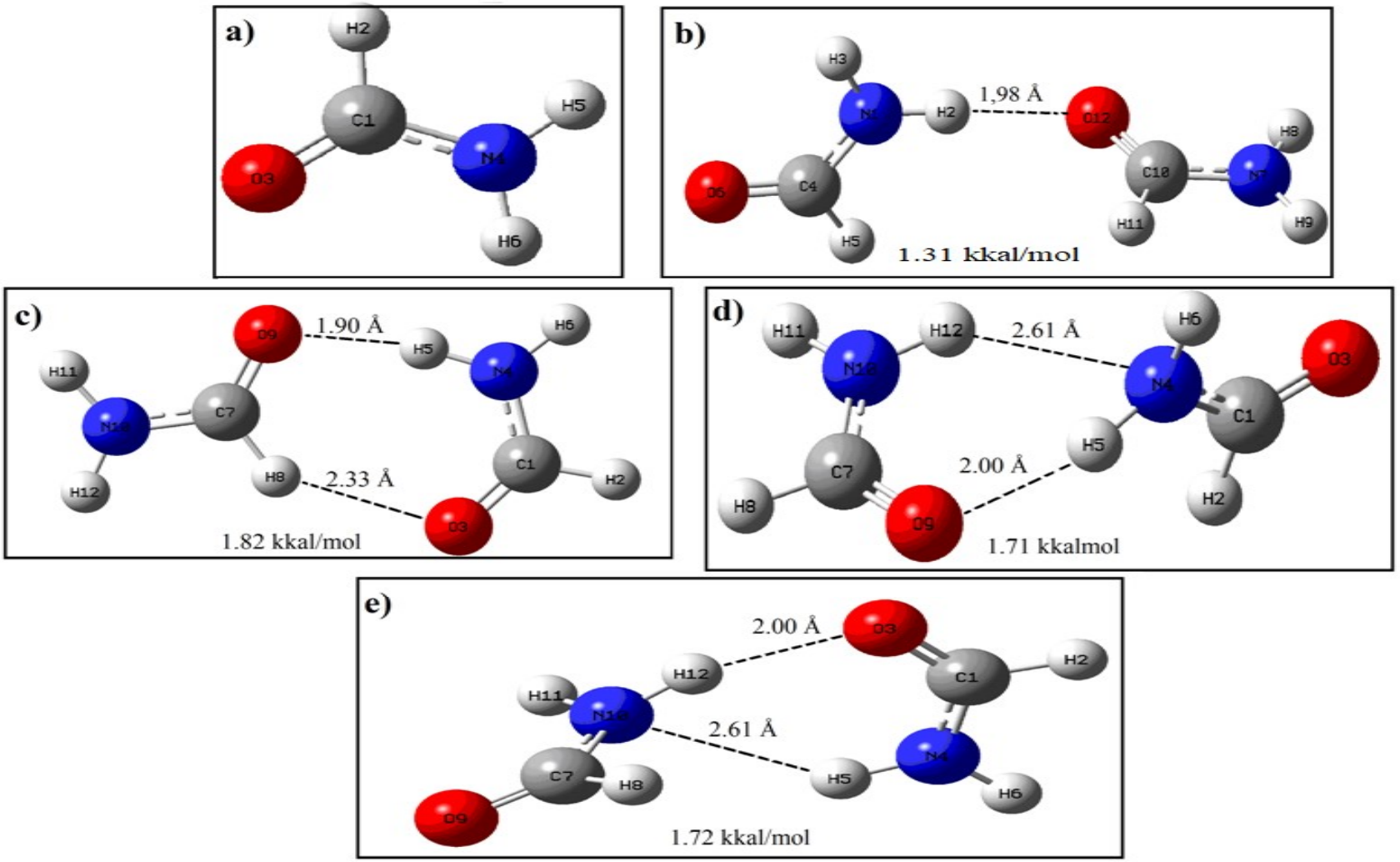

Figure 2. Monomer and dimmer aggregates of the formamide molecule

Figure 2 illustrates the results of the calculations for formamide molecule aggregates ranging from monomer to pentamer. The atoms in the molecule are numbered and the monomer of formamide is shown in part a) of Figure 2. The 3O and 4N atoms in the molecule are negatively charged, while the remaining atoms are positively charged. There is a high possibility that the O3 atom and the N2 atom have an internal hydrogen bond.

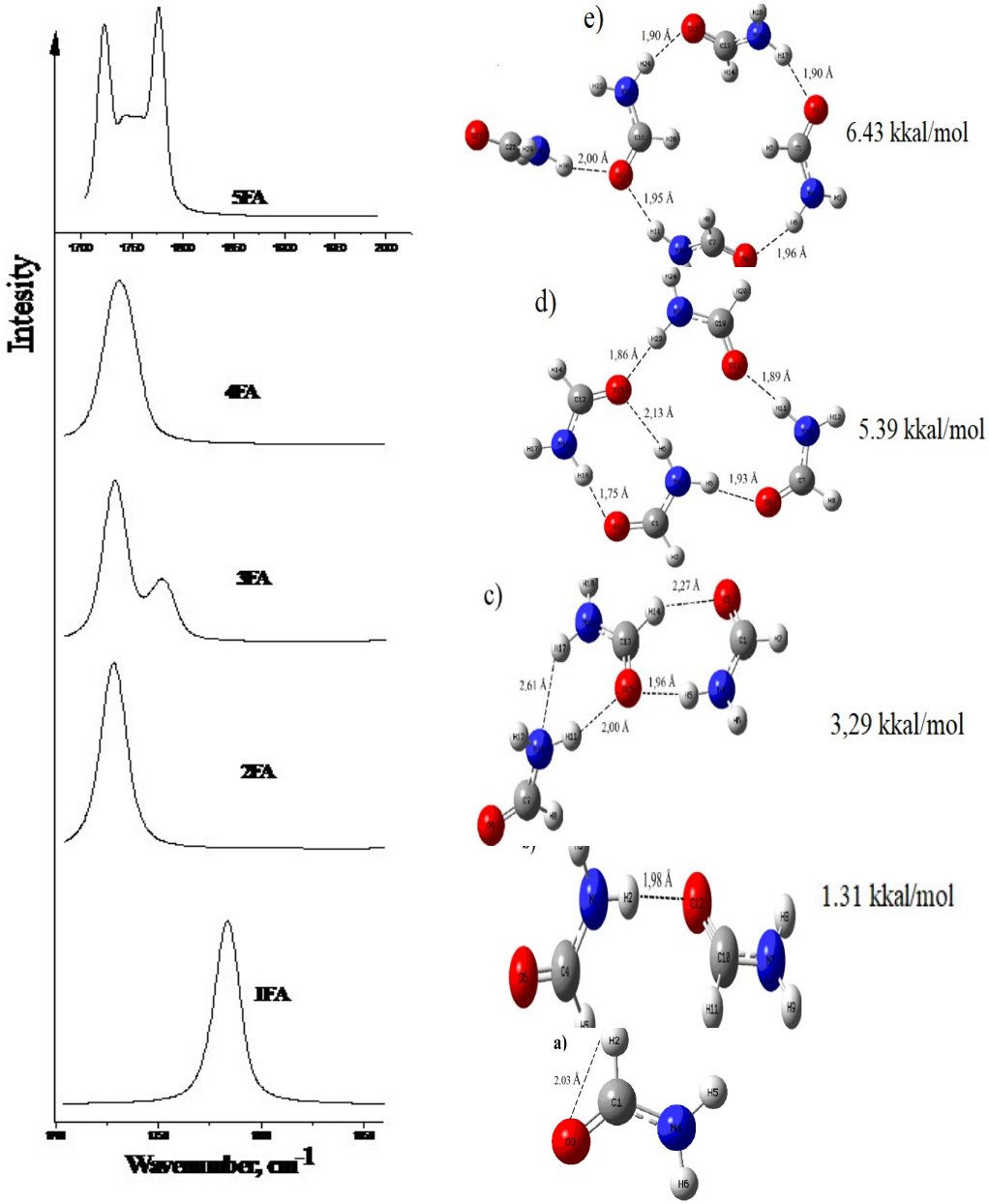

Figure 3. Aggregates of the formamide (FA) molecule and its corresponding Raman spectra

Figure 3 shows the aggregates of the formamide molecule from monomer to pentamer and the Raman spectra obtained in the calculation. Closed structural complexes are observed as a result of the formation of two different types of H-bonds in trimer formation. The distances between the atoms are: H14-O3 – 2.27 Å and H17-N10 – 2,61 Å , H5-O15 – 1,96 Å and H11-O15 – 2,00 Å. The charges of the atoms involved in these bonds also change. According to the calculations, the trimer's dipole moment is 4.2 D. The frequencies of the band corresponding to the compound C = O vibration are 1728 cm^{-1}, 1757 cm^{-1}, and 1764 cm^{-1}, and the energy of trimer formation is 3.29 kcal / mol.

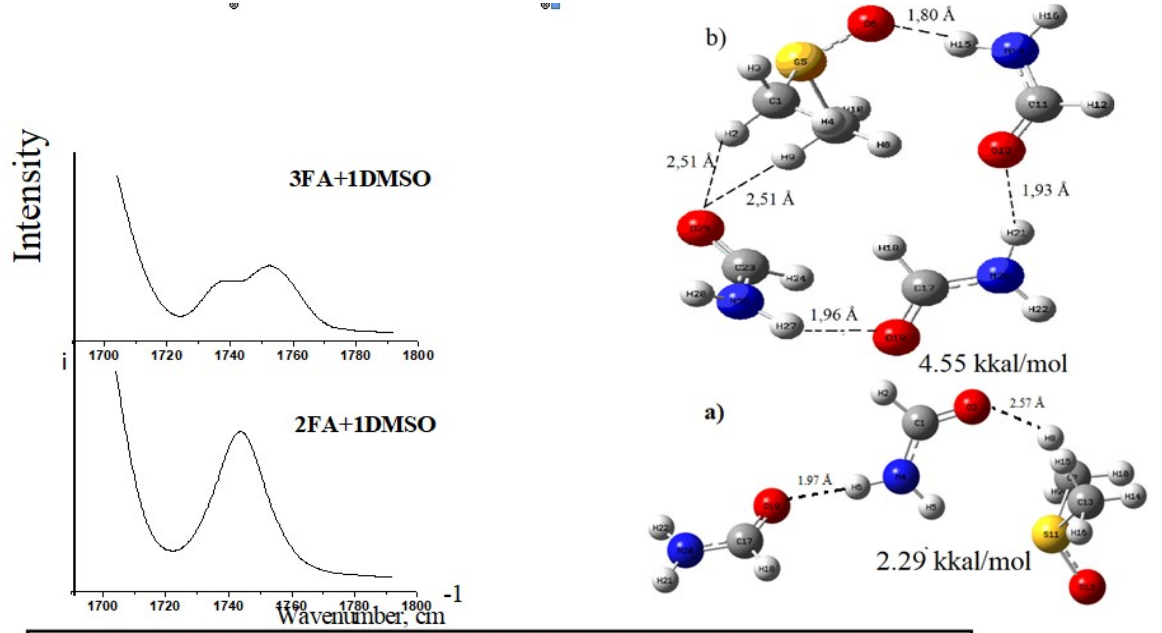

Figure 4. Aggregates of the FA and DMSO molecule and its corresponding Raman spectra

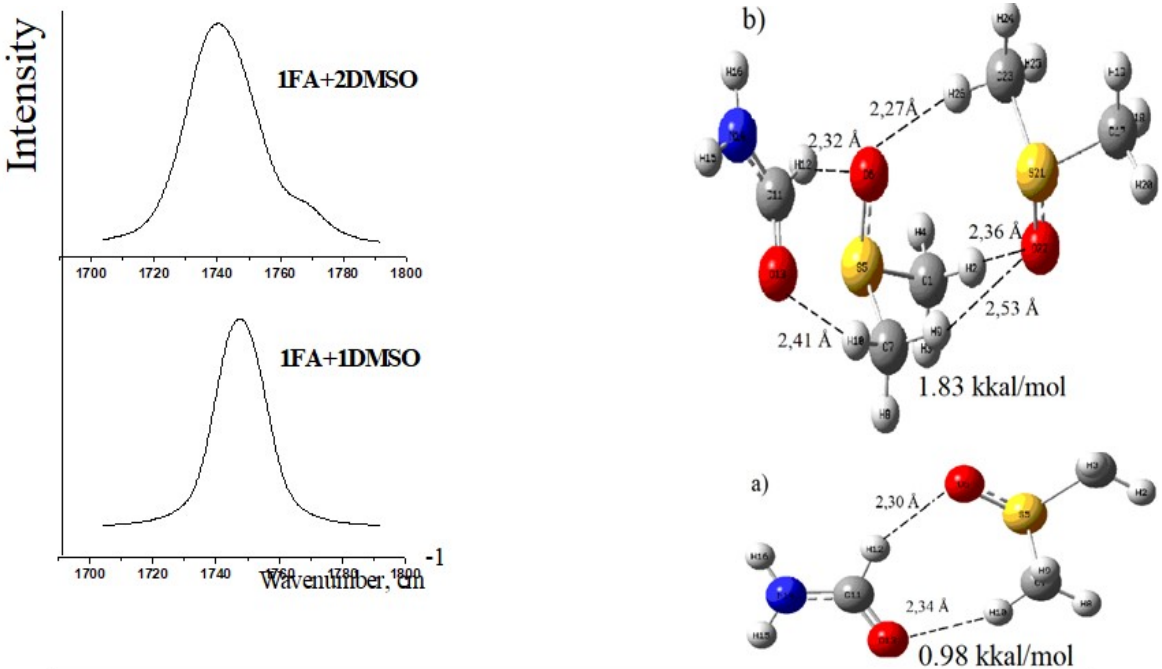

Figure 5. Aggregates of the FA and DMSO molecule and its corresponding Raman spectra

The solution of formamide with DMSO was also studied in this study (Figures 4 and 5). Theoretical calculations were performed for complex cases of this system. In dimer formation, the H12 atom of the formamide molecule's C-H group forms two different types of H-bonds with the O6 atom of the DMSO and the O13 atom of the formamide's C = O group with the H10 atom of the DMSO. The energy of formation of this type of dimer is 0.98 kcal / mol. The calculations were also carried out on one formamide molecule and two DMSO molecules. In the formation of such aggregates, 5 types of groups of interacting molecules participate in H-bonding. The formation energy of such an aggregate is 1.83 kcal / mol, and the average bond length is 2.30 Å.

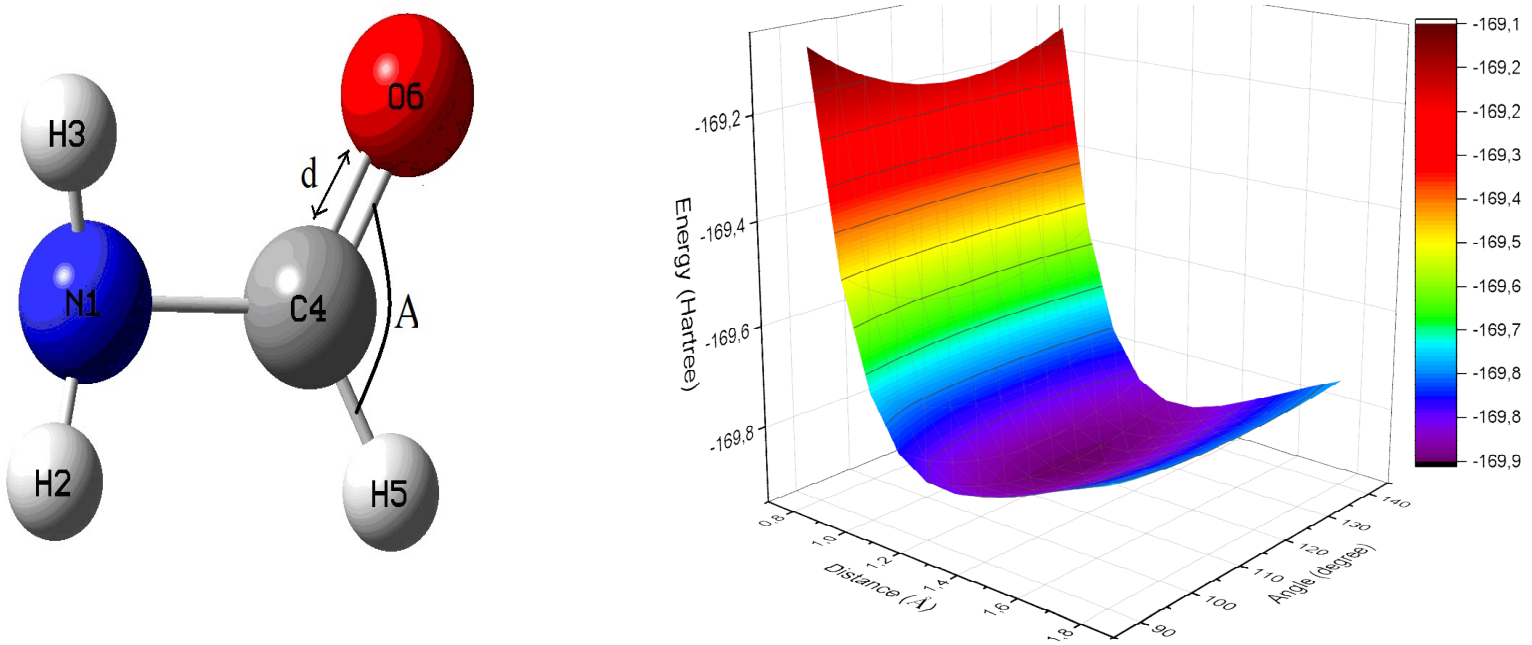

Figure 6. 3 D potential energy graph for FA monomer

Figure 6 shows a 3D graph of the energy dependence of the monomer of the formamide molecule and its angle (between O6-C4-H5) and distance (between C = O). The calculations show the dependence of the energy of the molecule being optimized on the distance between the atoms (0.8 Å to 1.8 Å) and the angle (90^0 to 140^0), respectively.

Conclusion

Formamide molecules form dimeric aggregates, according to experimental studies and calculations, and the formation of such dimers occurs not only as a result of the interaction of the molecules' charges, but also as a result of hydrogen bonds. Such hydrogen bonds are open dimers bound by an oxygen atom in the C=O group of the formamide through a hydrogen atom in the C-H group of the adjacent molecule, in which case a single C=O group of the formamide is freely bound. Closed type aggregates are formed as a result of two different hydrogen bonds in the formation of type 2 dimeric aggregates.

THANK YOU FOR ATTENTION